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Molecular Engineering of Side Chain Liquid Crystalline Polymers

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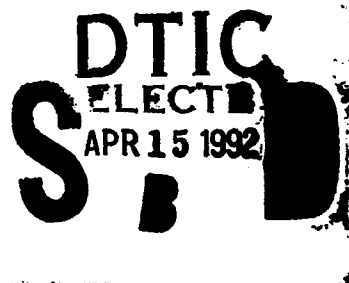Cleveland, OH 44106-2699

Submitted for Publication

DTIC
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APR 15 1992
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in

"Contemporary Topics in Polymer Science",
J. C. Salamone and J. Riffle Eds., Plenum Press, New York

March 27, 1992

92-09508

92   4 13 100

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
	Available for distribution
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 63	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Case Western Reserve University	4B566	ONR

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
2040 Adelbert Road Cleveland, OH 44106	Office of Naval Research Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
ONR		

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Office of Naval Research 800 N. Quincy Arlington, VA 22217	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO
	N00014-89	J-1828	413c024	

11. TITLE (Include Security Classification)
Molecular Engineering of Side Chain Liquid Crystalline Polymers in "Contemporary Topics in Polymer Science", J. C. Salamone and J. Riffle Eds., Plenum Press, New York

12. PERSONAL AUTHOR(S) Virgil Percec* and Dimitris Tomazos

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Preprint	FROM ____ TO ____	March 27, 1992	

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This chapter discusses the molecular engineering of side chain liquid crystalline polymers mainly by living polymerization reactions. According to thermodynamic schemes, the polymer effect through its molecular weight and backbone flexibility can provide an overall change of entropy of the system. Consequently it can transform virtual mesophases into monotropic and enantiotropic mesophases. The control of molecular weight provided by living cationic polymerization of mesogenic vinyl ethers can be used successfully to tailor-make phase transitions like smectic A (s_A), nematic (n) and re-entrant nematic (n_{re}) in side chain liquid crystalline polymers and copolymers. Some additional examples of molecular engineering of side chain liquid crystalline polymers containing crown ethers and polypodants and self-assemblying side chain liquid crystalline polymers are presented.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	unclassified/unlimited
22a. NAME OF RESPONSIBLE INDIVIDUAL Virgil Percec	**22b. TELEPHONE (Include Area Code)** (216) 368-4242 **22c. OFFICE SYMBOL**

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.
All other editions are obsolete.

MOLECULAR ENGINEERING OF SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

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SOME GENERAL CONSIDERATIONS ON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

The field of side chain liquid crystalline polymers was recently reviewed.[1] Therefore, this paper will discuss only recent progress made on their molecular engineering mainly by living polymerization reactions. Most of the present discussion will be made on side chain liquid crystalline polymers with mesogenic groups normally attached to the polymeric backbone.[2] Figure 1 outlines the concept of side chain liquid crystalline polymers. It has been theoretically predicted[3] that the conformation of the polymer backbone should get distorted in the liquid crystalline phase. Both small-angle neutron scattering (SANS) experiments[4-8] and X-ray scattering experiments,[9-11] have shown that the statistical random-coil conformation of the polymer backbone is slightly distorted in the nematic phase and highly distorted in the smectic phase.

Let us first consider very briefly the influence of various parameters (i.e., nature of flexible spacer and its length, nature and flexibility of the polymer backbone and its degree of polymerization) on the phase behavior of a side chain liquid crystalline polymer. According to some thermodynamic schemes which were described elsewhere,[12,13] the increase of the degree of polymerization decreases the entropy of the system and therefore, if the monomeric structural unit exhibits a virtual or monotropic mesophase, the resulting polymer should most probably exhibit a monotropic or enantiotropic mesophase. Alternatively, if the monomeric structural unit displays an enantiotropic mesophase, the polymer should display an enantiotropic mesophase which is broader. It is also possible that the structural unit of the polymer exhibits more than one virtual mesophase and therefore, at high molecular weights the polymer will increase the number of its mesophases. All these effects were observed with various polymer systems.[2]

The length of the flexible spacer determines the nature of the mesophase. Long spacers favor smectic phases while short spacers favor nematic phases. This effect is similar to that observed in low molar mass liquid crystals.

At constant molecular weight the rigidity of the polymer backbone determines the thermodynamic stability of the mesophase. According to the thermodynamic schemes described previously[12,13] the isotropization temperature of the polymer with more rigid backbone should be higher. However, experimentally this situation is reversed. The highest isotropization transition temperature is observed for polymers with more flexible backbones. This conclusion is based on systematic investigations performed with two mesogenic groups which are constitutional isomers i.e., 4-methoxy-4'-hydroxy-α-methylstilbene (4-MHMS)[14] and 4-hydroxy-4'-methoxy-α-methylstilbene (4'-MHMS)[15] and polymethacrylate,
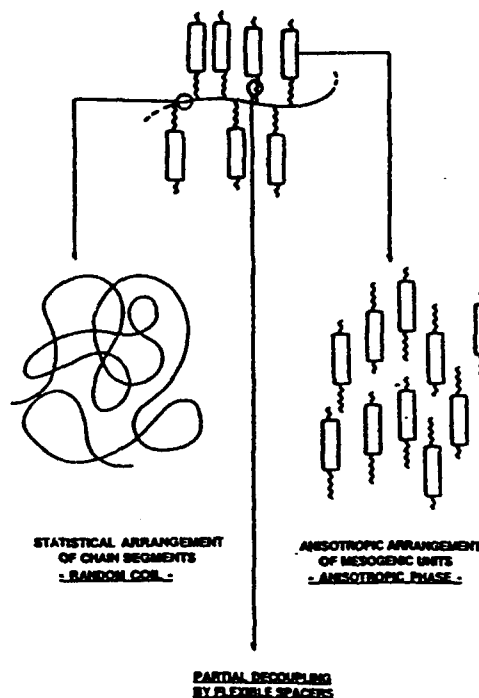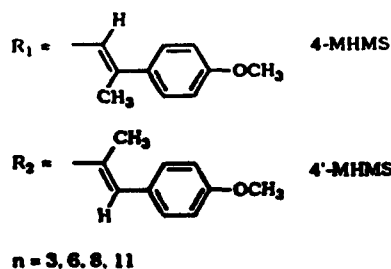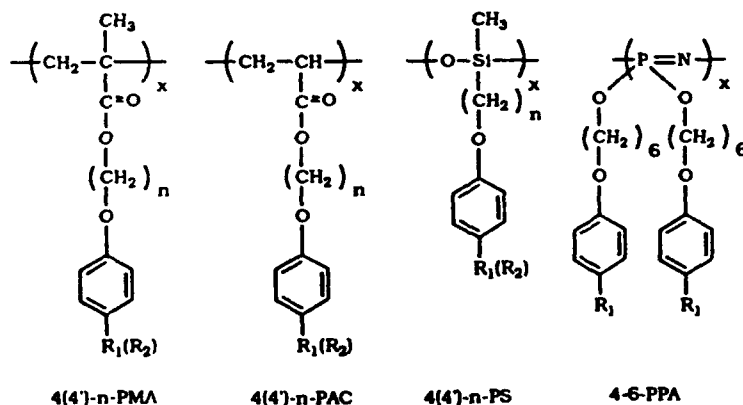
Figure 1. Schematic representation of side chain liquid crystalline polymers showing the necessity of decoupling the mesogenic groups and the polymer backbone through flexible spacers.

Scheme 1. Polymethacrylates, polyacrylates, polysiloxanes and polyphosphazene based on 4-MHMS and 4'-MHMS constitutional isomeric mesogenic groups.

polyacrylate, polysiloxane and polyphosphazene backbones[14-16] (Scheme 1). This dependence can be explained by assuming that a more flexible backbone uses less energy to get distorted and therefore, generates a more decoupled polymer system. In fact the more flexible backbones do not generate only higher isotropization temperatures but also a higher ability towards crystallization. However, contrary to all expectations the entropy change of isotropization is higher for those polymers which are based on more rigid backbones and therefore, exhibit lower isotropization temperatures (Figure 2a,b).[17] This contradiction between the values of the entropy change and the isotropization temperatures can be accounted for by a different mechanism of distortion of different polymer backbones as outlined in Figure 3. That is, while a rigid backbone gets more extended and therefore, in the smectic phase it can cross the smectic layer, in the case of a flexible backbone it gets squeezed between the smectic layers. The higher configurational entropy of the flexible backbone versus that of the rigid backbone in the smectic phase can account for the difference between the entropy change of isotropization from Figure 2. At shorter spacer lengths, there is not much difference between the contribution of various backbone flexibilities since most probably, in order to generate a mesophase they should get extended. Therefore the entropy change of isotropization is less dependent of backbone flexibility (Figure 2).
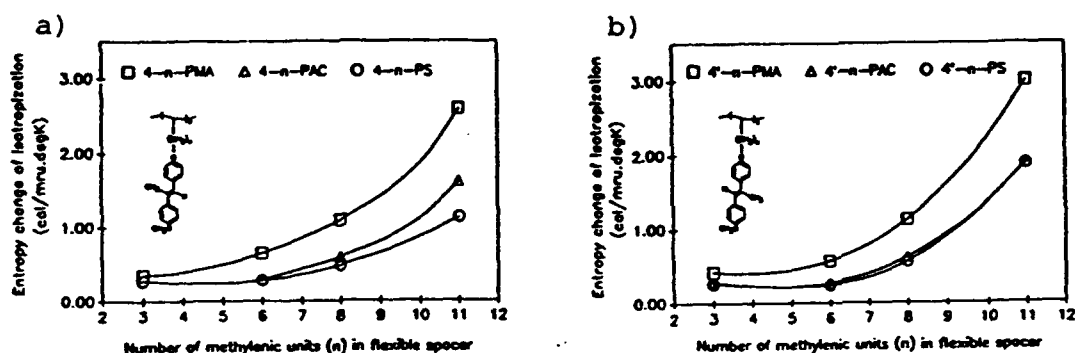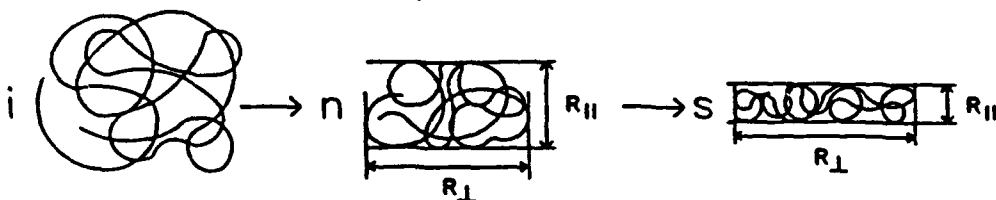

Figure 2. a) The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4-MHMS isomer.

b) The dependence between the entropy change of isotropization (ΔS_i) determined from the cooling DSC scans, the nature of the polymer backbone and the number of methylenic units (n) in the flexible spacer for the series of polymers based on 4'-MHMS isomer.

Based on this discussion it is quite obvious that copolymers containing structural units with and without mesogenic groups and flexible backbone display a microphase separated morphology in their smectic phase (Figure 4).[2,9,11] Therefore, the highest degree of decoupling is expected for copolymers containing mesogenic and nonmesogenic structural units and highly flexible backbones, i.e., microphase separated systems. In this last case, when the monomeric structural unit of the polymer exhibits a virtual mesophase, the high molecular weight polymer might also display only a virtual or a monotropic mesophase. The transformation of a virtual and/or monotropic mesophase of the homopolymers into an enantiotropic mesophase can be most conveniently accomplished by making copolymers based on two monomers which are constitutional isomers, such as monomers based on 4-MHMS and 4'-MHMS.[18,19] Since the structural units of the homopolymers based on 4-MHMS and 4'-MHMS are isomorphic within their liquid crystalline phase, but not within their crystalline phase, the crystalline melting transition decreases while the mesophase exhibits a continuous almost linear dependence on composition. As a consequence, the virtual or monotropic mesophase of the homopolymer becomes enantiotropic.[18,19] Finally, the molecular weight at which the isotropization temperature becomes independent of molecular weight should be, and indeed is, dependent on the flexibility of the polymer backbone. For example, the isotropization temperature of polysiloxanes[20,21] containing mesogenic side groups is molecular weight dependent up to much higher molecular weights than that of polymethacrylates containing mesogenic side groups.[2]

a Theoretical (M. Warner)

b Experimental (Saclay Group)

$$R_{II PAC} \leqslant R_{II PMA} \qquad R_{II PAC} < L_{PAC} \qquad R_{II PMA} \geqslant L_{PMA}$$
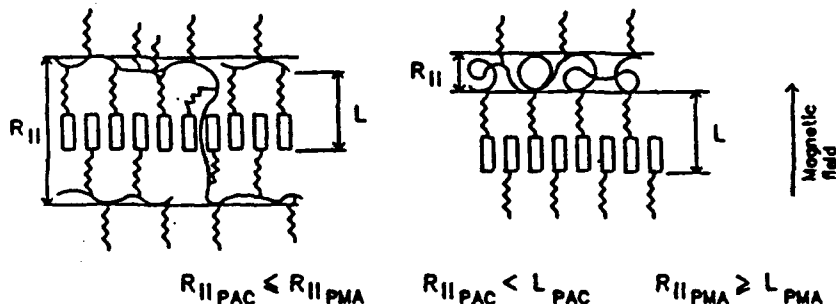
Figure 3. a) Schematic representation of the theoretical distortion of the statistical random-coil conformation of the polymer backbone in the nematic and smectic phases; b) Two possible modes of distortion of the random-coil conformation of a rigid (left) and a flexible (right) polymer backbone. R_{II} refers to the radius of gyration paralled to the magnetic field. The radius of gyration perpendicular to the magnetic field is labelled as $R_\perp$.

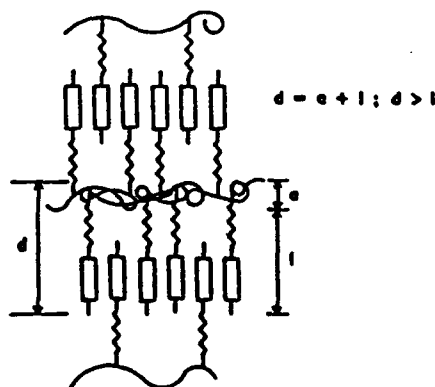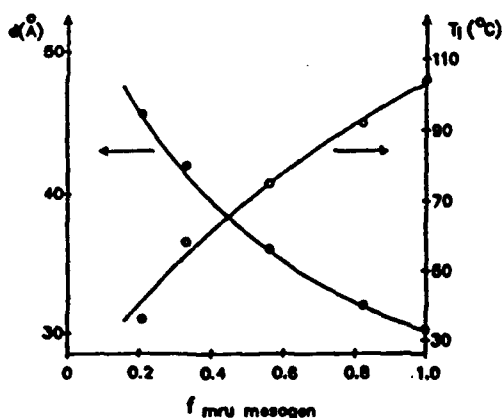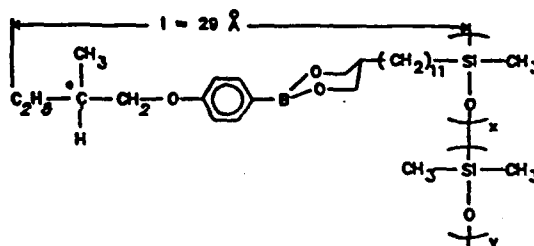| mesogen(%)	d(Å)	e(Å)	Ti(°C)
100	30.4	1.4	104
82	32.0	3.0	92
56	36.0	7.0	75
33	42.0	13.0	58
21	45.6	16.6	36

Figure 4. Microphase separated morphology of smectic copolymers.

Based on this discussion and on the thermodynamic discussion described previously,[12,13] we can easily consider that the "polymer effect" can provide via its molecular weight and backbone flexibility the same effect. In an oversimplified way it can be considered that it provides an overall change in the entropy of the system. Through this change, it can transform, in a reversible way, a virtual mesophase into a monotropic and subsequently into an enantiotropic one. In addition, the kinetic factors provided by the glass transition and crystallization should always be considered. For example, the formation of a mesophase located in the close proximity of a glass transition temperature becomes kinetically controlled or even can be kinetically prohibited.

MOLECULAR ENGINEERING OF LIQUID CRYSTALLINE POLYMERS BY LIVING POLYMERIZATION

General Considerations

Several polymerization methods were investigated in order to develop living polymerization procedures for the preparation of side chain liquid crystalline polymers with well defined molecular weight and narrow molecular weight distribution. They include cationic polymerization of mesogenic vinyl ethers,[22,23] cationic ring opening polymerization of mesogenic cyclic imino ethers,[24] group transfer polymerization of mesogenic methacrylates,[25-28] and polymerization of methacrylates with methylaluminium porphyrin catalysts.[29] Cationic polymerization has been proved to be the most successful since it can be used to polymerize under living conditions mesogenic vinyl ethers containing a large variety of functional groups.[30-51] Scheme 2 provides some representative examples of mesogenic vinyl ethers which could be polymerized by a living mechanism with our preferred initiating system (i.e., CF_3SO_3H, $(CH_3)_2S$, CH_2Cl_2, 0 °C).[52] As we can observe from Scheme 2, vinyl ethers containing nucleophilic groups such as methoxybiphenyl,[44] electron-withdrawing groups such as cyanobiphenyl,[30-35,44,45] nitrobiphenyl and cyanophenylbenzoate,[44] double bonds like in 4-alkoxy-α-methylstilbene,[46] double bonds and cyano groups like in 4-cyano-4'-α-cyanostilbene,[34] aliphatic aromatic esters,[36] acidic protons and perfluorinated groups,[44,47] oligooxyethylene and aromatic ester groups,[49] crown
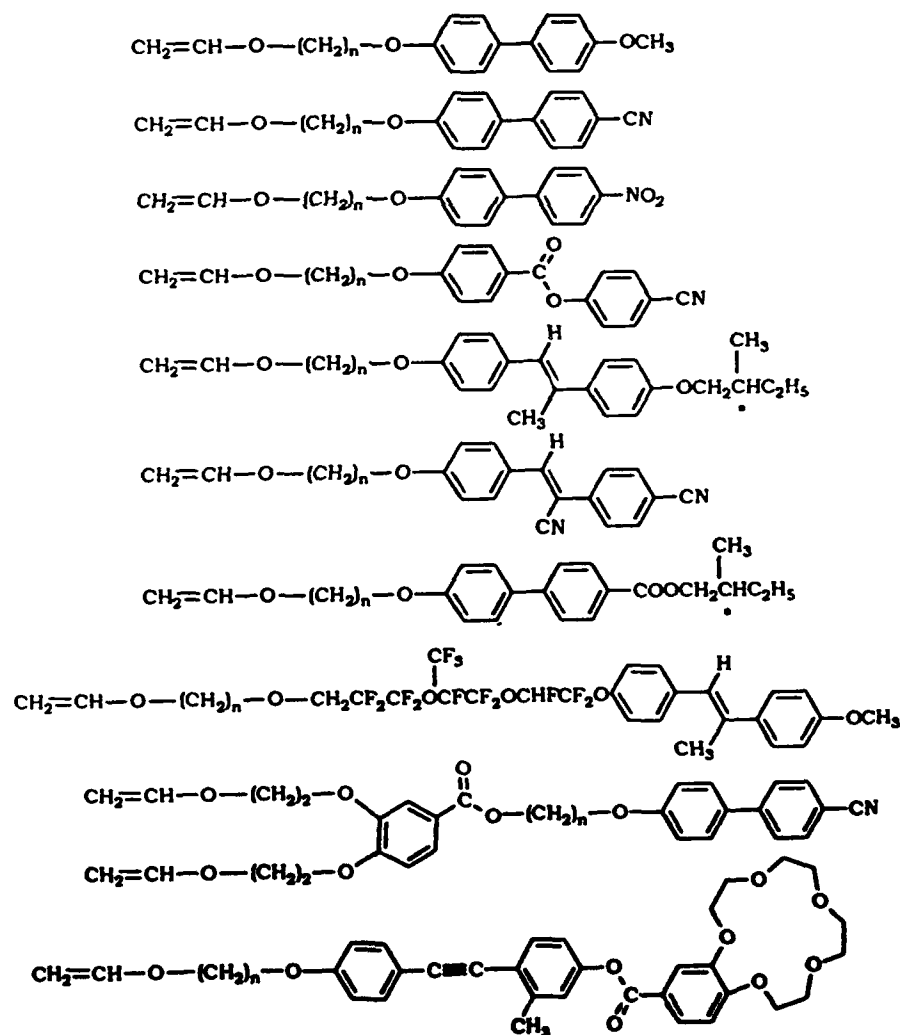

Scheme 2. Representative examples of mesogenic vinyl ethers which can be polymerized by living cationic mechanism.

ethers and triple bonds,[50] all can be polymerized by a living cationic mechanism. In addition, cationic polymerization of any of these monomers can be performed in melt phase either in liquid crystalline phase or in isotropic phase by using thermal[53], or photo cationic initiators.[54,55] When the polymerization is performed in liquid crystalline phase with alligned films of liquid crystalline monomers, perfectly alligned single crystal liquid crystalline polymer films are obtained.[54,55] In the following two subchapters we will discuss two topics. The first one refers to the influence of molecular weight on the phase transitions of poly{ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ether}s with alkyl groups containing from four to eleven methylene units. In the second one we will demonstrate the molecular engineering of phase transitions of side chain liquid crystalline polymers by azeotropic living copolymerization experiments.

Influence of Molecular Weight on the Phase Transitions of Poly{ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ether}s

Scheme 3 outlines the general method used for the synthesis of ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ethers (6-n) and of the model compound for the polymer with degree of polymerization of one i.e., ω-[(4-cyano-4'-biphenylyl)oxy]alkyl ethyl ethers (8-n). We will use over the entire discussion the same short notations as in the original publications. The synthesis and characterization of poly(6-n) and (8-n) with n = 2, 3, 4,[31] 5, 7,[32] 6, 8,[44] 9, 10,[33] and 11[30] will be briefly discussed. Details are available in the original publications. All polymers have polydispersities of about 1.10. Scheme 4 outlines the polymerization mechanism and the structure of the resulted polymers. This structure was confirmed by 300 MHz 1-D and 2-D ^{1}H-NMR spectroscopy.[56]
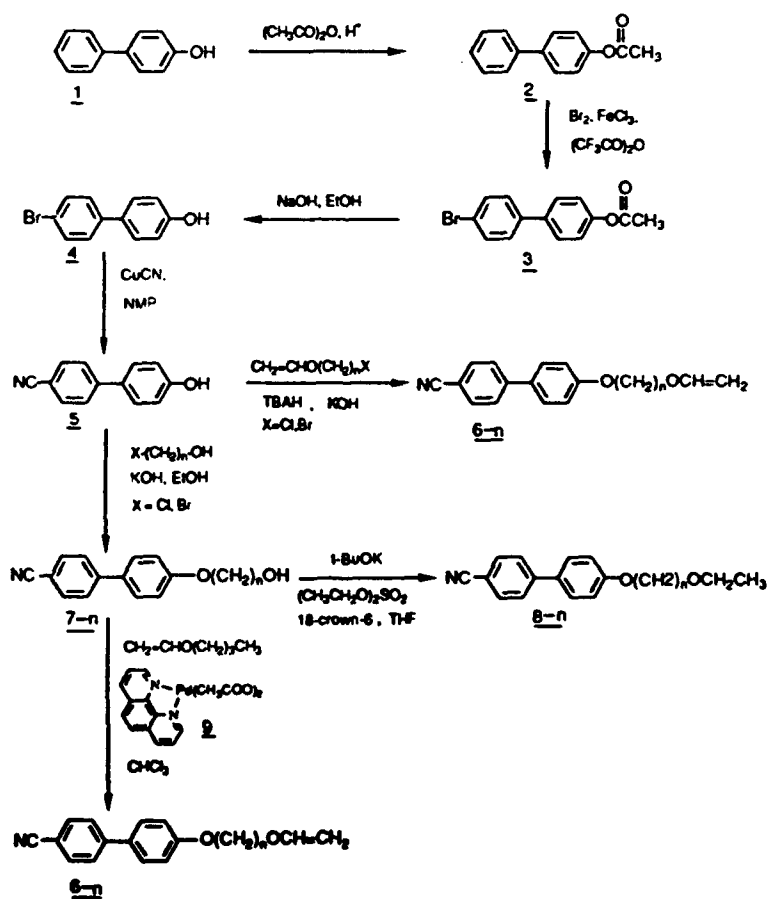
Scheme 3. Synthesis of ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ethers (6-n).
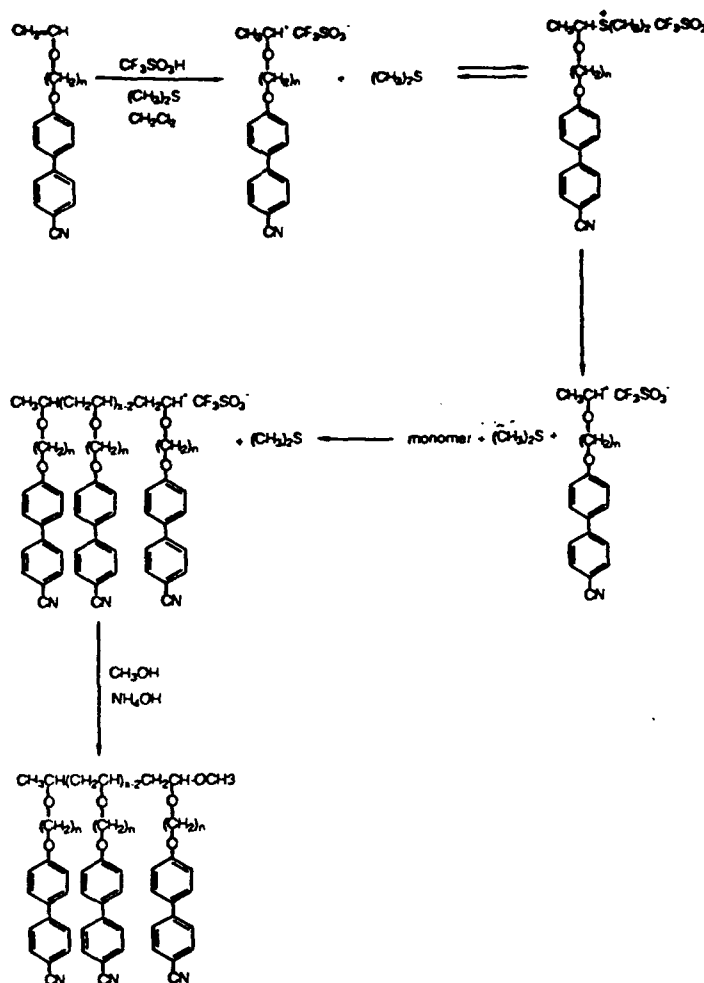
Scheme 4. Mechanism of living cationic polymerization of ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ethers (6-n).

All data were classified according to their similarities. Figure 5 presents the dependence of phase transition temperatures of poly(6-n) with n = 3, 4, 7 and 9 as a function of molecular weight. These data were collected from second heating scans. The data for 8-n are not plotted . 8-3 is crystalline, 8-4 and 8-7 exhibit a monotropic nematic mesophase while 8-9 monotropic nematic and smectic mesophases. As we can observe from Figure 5 by increasing the molecular weight all four polymers show a broadening of the thermal stability of their mesophase. The mesophase of 8-7 and 8-9 changes from nematic to s$_A$ by increasing the degree of polymerization from one to about 3.

Figure 6 presents similar data for poly(6-2), poly(6-6) and poly(6-8). In all cases the nature of the mesophase is molecular weight dependent. Poly(6-2) has a nematic mesophase only at degrees of polymerization lower than 5. 8-2 is only crystalline. At degrees of polymerization higher than 5, poly(6-2) is only glassy. This is because its glass transition temperature becomes higher than the isotropization temperature and therefore, the mesophase is kinetically prohibited. 8-6 exhibits an enantiotropic nematic mesophase. At low degrees of polymerization poly(6-6) and poly(6-8) exhibit nematic and s$_A$ mesophases. Due to the difference between the slope of the dependences of the nematic phase transition temperature on molecular weight and of the s$_A$ phase transition temperature on molecular weight, above a certain molecular weight the nematic phase disappears. Both poly(6-6) and poly(6-8) show a second smectic mesophase (s$_X$, i.e. unassigned). Qualitatively, this behavior is in agreement with the influence of molecular weight on phase transitions predicted by thermodynamics.[12,13] Quantitative predictions of these phase diagrams require more theoretical research.
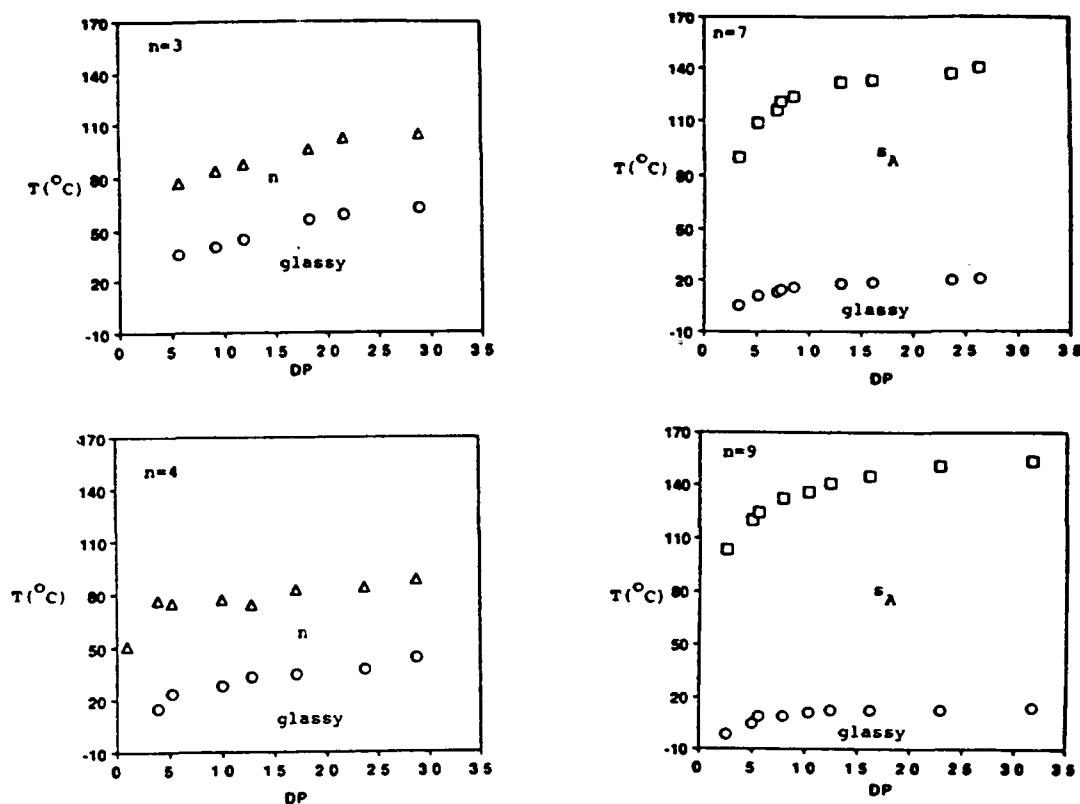
Figure 5. The influence of molecular weight on the phase behavior of poly(6-3), poly(6-4), poly(6-7) and poly(6-9) (determined from second DSC heating scans).

Finally, Figure 7 presents the behavior of poly(6-5), poly(6-10) and poly(6-11). 8-5 shows an monotropic nematic phase, 8-10 a monotropic s_A phase while 8-11 an enantiotropic s_A mesophase. Poly(6-5) exhibits above a degree of polymerization of 10 the unusual sequence isotropic-nematic-s_{Ad}-n_{re}-glassy.[57] This will be discussed in more detail in a subsequent subchapter. At high molecular weights poly(6-10) and poly(6-11) exhibit s_A and s_X phases.

As a general observation we can mention that polymers with short spacers (n = 2, 3, 4) and medium length spacers containing an odd number of methylene units (n = 7, 9) do not generate polymorphism at different molecular weights. Polymers with medium length and an even number of methylene units (n = 6, 8), as well as polymers with long length with both even and odd numbers of methylenic units (n = 10, 11) generate a rich polymorphism which is molecular weight dependent. The borderline polymer is poly(6-5) which is the only one displaying n and s_A mesophases over a broad range of molecular weights and therefore, also generates the reentrant nematic mesophase.[57]

Molecular Engineering of Liquid Crystalline Phases by Living Cationic Copolymerization

In order to tailor make mesophases of side chain liquid crystalline copolymers we first need to synthesize copolymers with constant molecular weight and controllable composition. Copolymer composition is conversion dependent in all statistic copolymerizations. The only exception is provided by azeotropic copolymerizations in which the copolymer composition is identical to the monomer feed at any conversion.[58] This situation is provided by monomers with $r_1 = r_2 = 1$. Since the reactivity of the polymerizable vinyl ether groups is not spacer length dependent, all 6-n monomers have the same reactivity. Therefore, all 6-n pairs of monomers lead to azeotropic copolymerizations, and when the copolymerization is performed under living conditions they lead to copolymers with controllable molecular weight. The azeotropic copolymerization of various pairs of 6-n monomers is outlined in Scheme 5. We will discuss selected examples of copolymers prepared from monomer pairs which give rise to homopolymers exhibiting nematic and nematic, s_A and s_A, nematic and s_A, and glassy and s_A phases as their highest temperature mesophases.
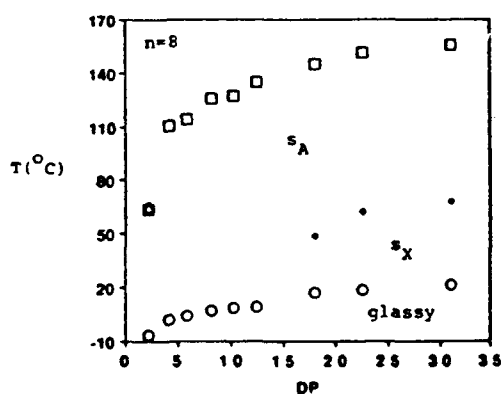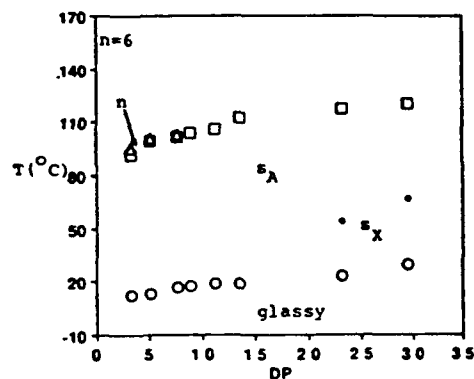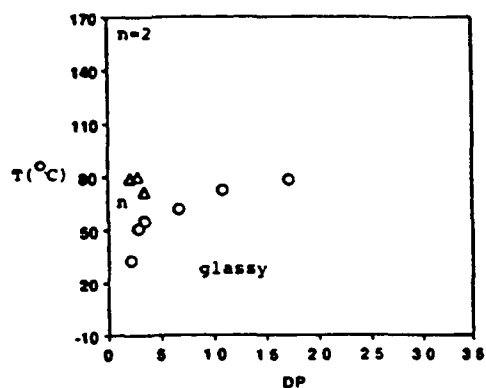
Figure 6. The influence of molecular weight on the phase behavior of poly(6-2), poly(6-6) and poly(6-8) (determined from second DSC heating scans).
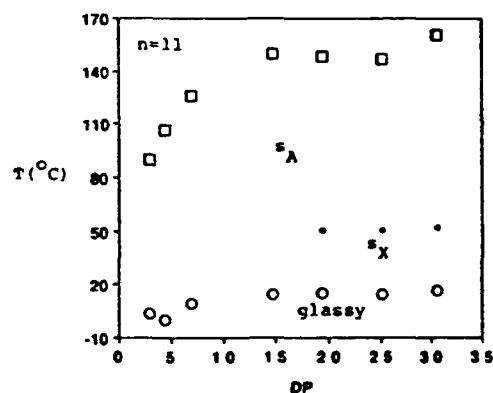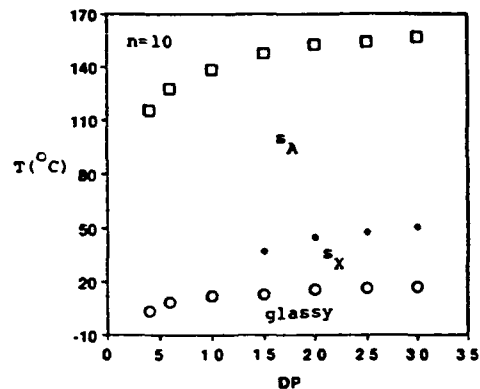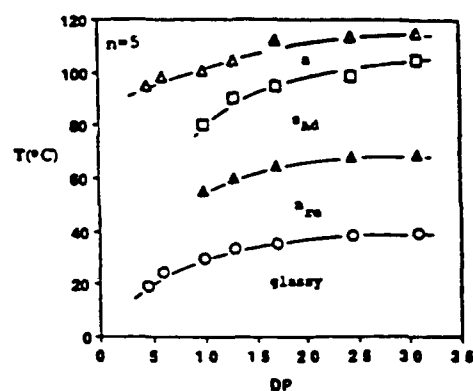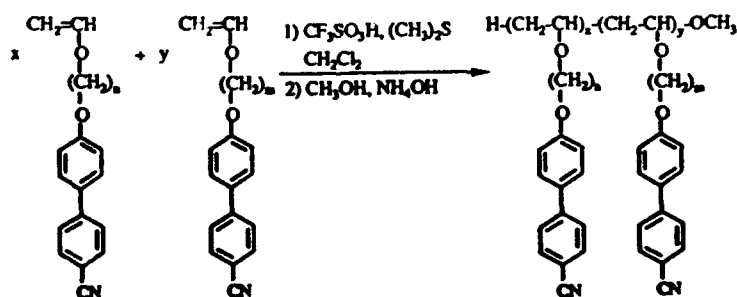
Figure 7. The influence of molecular weight on the phase behavior of poly(6-5), poly(6-10) and poly(6-11) (determined from second DSC heating scans).

Scheme 5. Azeotropic copolymerization of ω-[(4-cyano-4'-biphenylyl)oxy]alkyl vinyl ether (6-n) monomer pairs.

Figure 8 presents the dependence of phase transition temperatures obtained from second DSC heating scans (a,d), cooling scans (b, e) and the enthalpy changes associated with the highest temperature mesophase of copolymers poly[(6-3)-co-(6-5)]X/Y and poly[(6-6)-co-(6-11)]X/Y. The degrees of polymerization of all copolymers are equal to 20.[59] Copolymers poly[(6-3)-co-(6-5)]X/Y are based on a monomer pair which gives rise to two homopolymers displaying an enantiotropic nematic mesophase as their highest temperature mesophase. As we can observe from Figure 8a,b,c the nematic-isotropic transition temperature and its associated enthalpy change show linear dependences of composition. This means that the structural units derived from poly(6-3) and poly(6-5) are isomorphic into their nematic mesophase. However, the same two structural units are isomorphic within the s_A mesophase exhibited by poly(6-5) only over a very narrow range of compositions. The linear dependence of the isotropization temperature is predictable by the Schroeder-Van Laar equations.[60] The same discussion is valid for the copolymer system poly[(6-6)-co-(6-11)]X/Y except that the isotropization temperature of these copolymers exhibit an upward curvature. This upward curvature is also predicted by the Schroeder-Van Laar equations[60] and is due to the more dissimilar enthalpy changes associated with the isotropization temperatures of the two homopolymers.

Figure 9 presents the phase diagrams of copolymers poly[(6-3)-co-(6-11)]X/Y[57,59] and poly[(6-5)-co-(6-11)]X/Y.[57] Both sets of copolymers have degrees of polymerization of 20. Both pairs of copolymers are based on monomers which give rise to homopolymers exhibiting nematic and s_A as their highest temperature mesophases. However, poly(6-5) displays a nematic and a s_A mesophase, while poly(6-3) only a nematic mesophase. Both sets of copolymers display continuous dependences of their highest temperature mesophase with a triple point at a certain composition. This triple point generates over a very narrow range of compositions copolymers exhibiting the sequence isotropic-nematic-s_A-n_{re}. Again the shape of the dependences of the phase transition temperature on composition obeys the Schroeder-Van Laar equations.[60]

Figure 10 presents two sets of phase diagrams obtained from monomer pairs giving rise to homopolymers which exhibit isotropic and s_A mesophases as their highest temperature mesophases, i.e., poly[(6-2)-co-(6-8)]X/Y with degree of polymerization of 10,[61] and poly[(6-2)-co-(6-11)]X/Y with degree of polymerization of 15.[62] Both sets of copolymers display a similar phase diagram. Over a certain range of compositions the two structural units are isomorphic within the s_A phase, after which follows a triple point. After this triple point the two structural units are isomorphic within a newly generated nematic mesophase. Both copolymers generate within a certain range of compositions on the left side of the triple point the sequence isotropic-nematic-s_A-n_{re}.[57] Again the shape of the dependence of the highest temperature mesophase on composition is predictable by the Schroeder-Van Laar equations. This means that the stuctural units of all binary copolymers based on an identical mesogenic unit but different spacer lengths behave as an ideal solution. This behavior allows the engineering of mesomorphic phase transition temperatures and of their thermodynamic parameters in a straight forward manner by living azeotropic copolymerizations. The same behavior was demonstrated for monomer pairs which both give rise to homopolymers exhibiting a chiral smectic C mesophase.[63]

Side Chain Liquid Crystalline Polymers Exhibiting a Reentrant Nematic Mesophase

The reentrant nematic phase (n_{re}) was discovered in 1975 in low molar mass liquid crystals.[64] Since then it has received substantial theoretical and experimental interest.[65-73]

The first side chain liquid crystalline polymers exhibiting a n_{re} phase were reported in 1986.[74,75] Some other examples of polymers exhibiting the sequence isotropic-nematic-s_{Ad}-n_{re} were reported in the meantime.[57,76,77-80] All these polymers are based on mesogenic units containing a cyano group, five or six atoms in the flexible spacer and a polyacrylate or polyvinyl ether backbone. The replacement of these quite flexible backbones with a more rigid one like polymethacrylate does not allow the formation of the n_{re} phase. As discussed in the previous subchapter a n_{re} mesophase can be generated by copolymerization of two monomers which lead to homopolymers with nematic or isotropic and s_A as their highest temperature mesophases, since these copolymers exhibit a triple point on their phase

Figure 8. The dependence of phase transition temperatures obtained from second heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[((6-3)-co-(6-5)]X/Y and poly[((5)-co-(6-11)]X/Y (all with degrees of polymerization equal to 20).
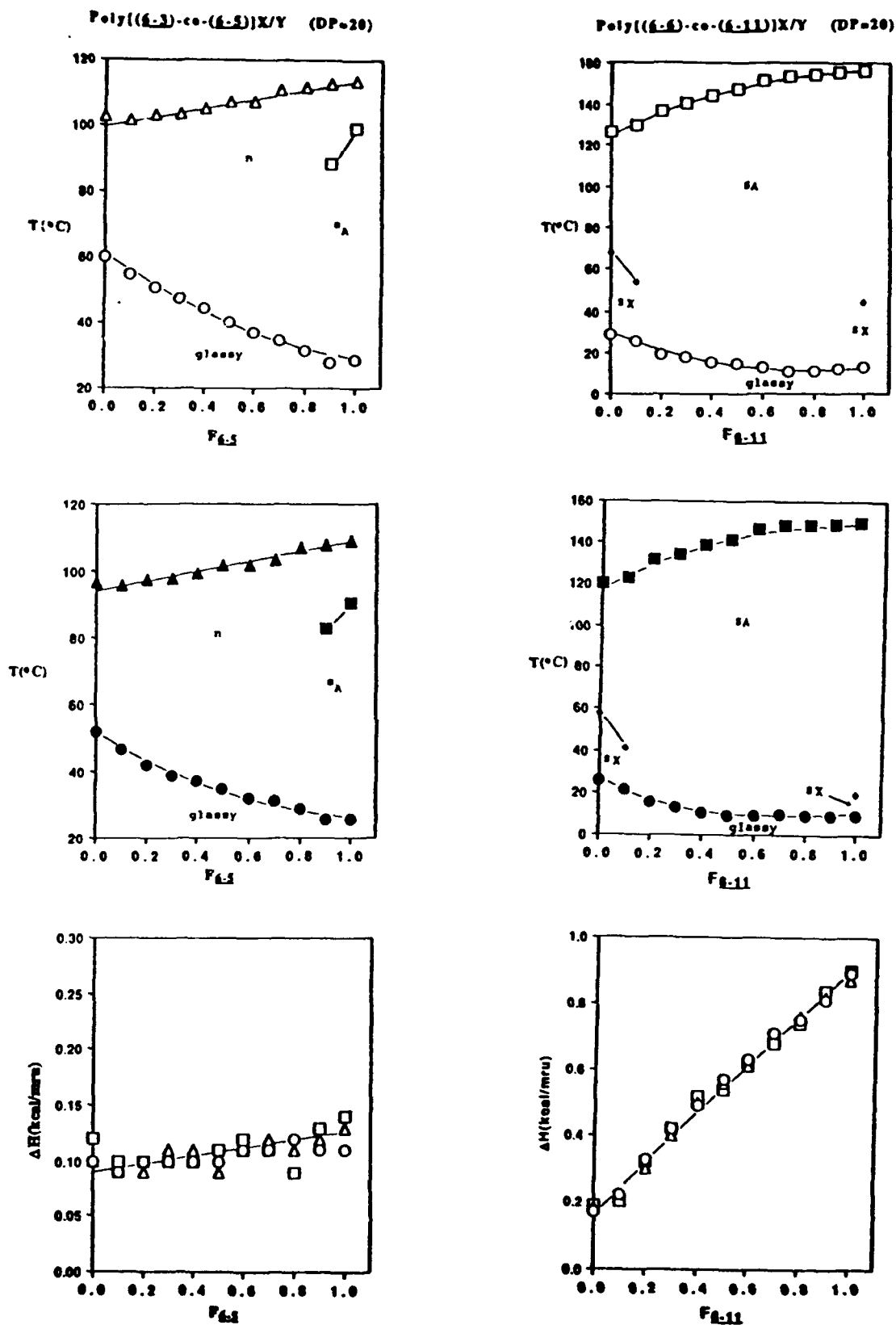
Figure 9. The dependence of phase transition temperatures obtained from second heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with their highest temperature mesophase of copolymers poly[(6-3)-co-(6-11)]X/Y and poly[(6-5)-co-(6-11)]X/Y (all with degrees of polymerization equal to 20).

Poly[(6-2)-co-(6-8)]X/Y   (DP=10)   Poly[(6-2)-co-(6-11)]X/Y   (DP=15)
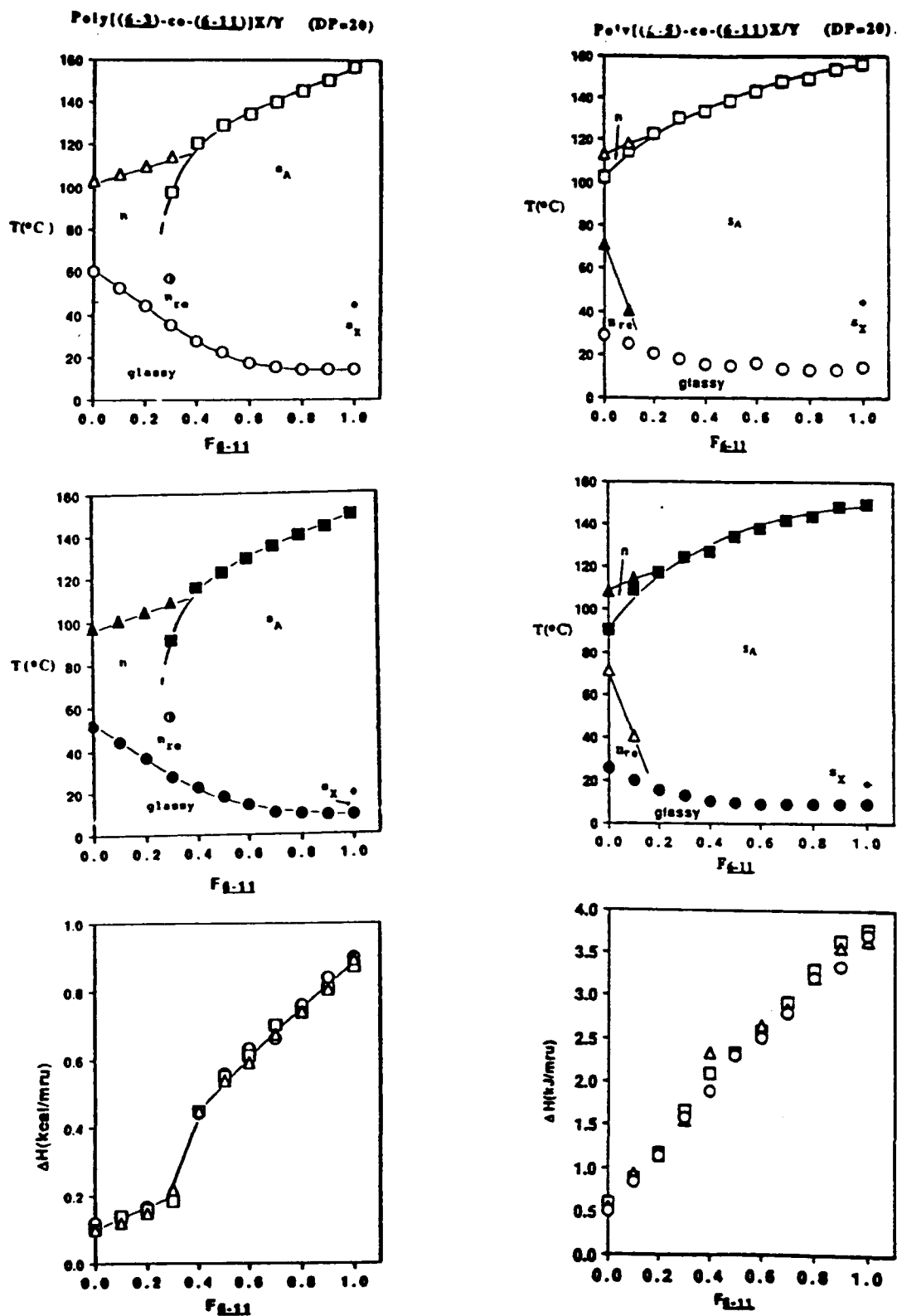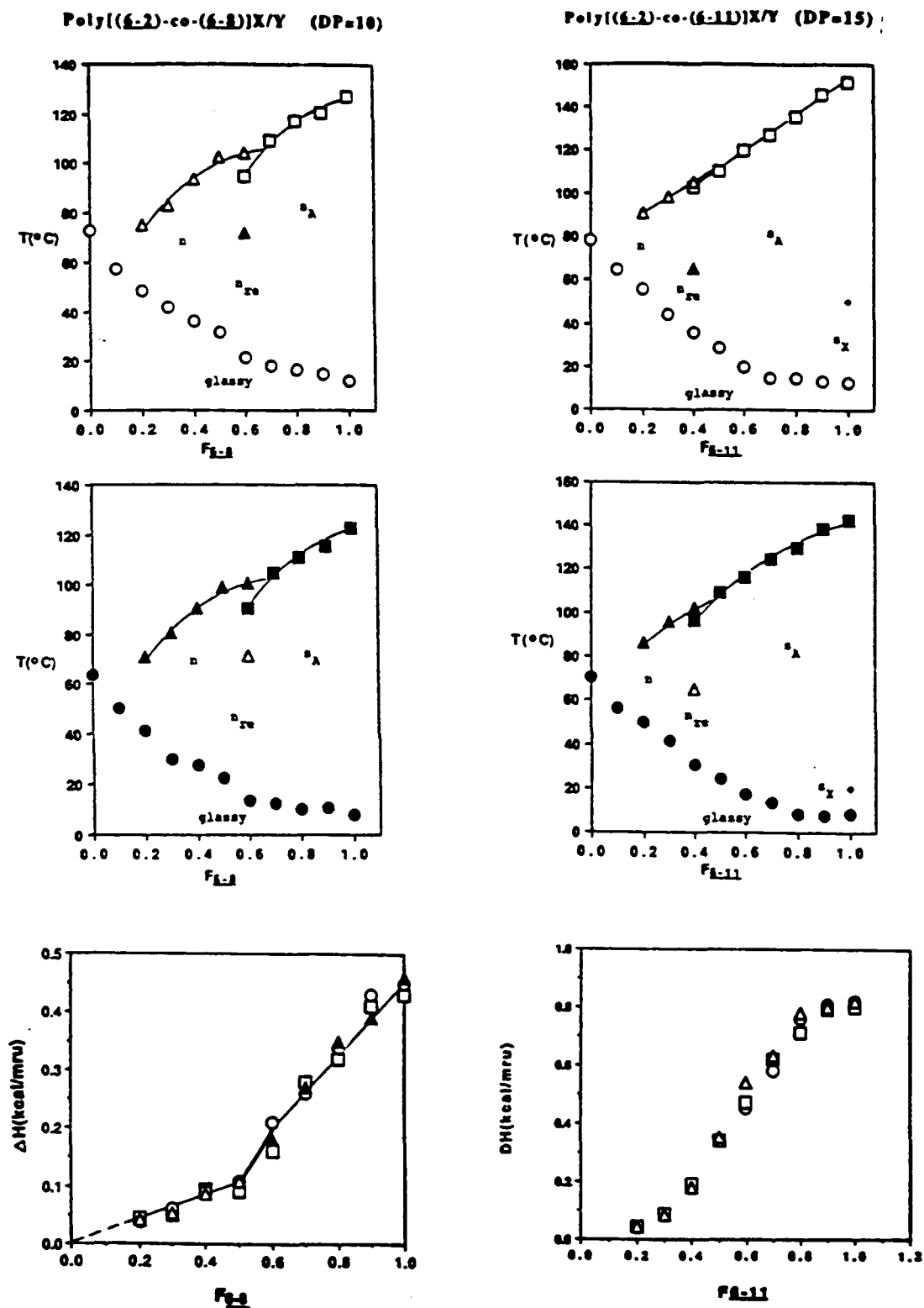

Figure 10. The dependence of phase transition temperatures obtained from second DSC
            heating scan (a,d), cooling scan (b,e), and the enthalpy changes associated with
            their highest temperature mesophase of copolymers poly[(6-2)-co-(6-8)]X/Y
            and poly[(6-2)-co-(6-11)]X/Y (with degrees of polymerization equal to 10 and
            15, respectively).

diagrams.[57] According to our experimental results any polymer which exhibits the sequence isotropic-nematic-s_A should also display a n_{re} phase. The most probable mechanism for the generation of a n_{re} phase is outlined in Figure 11.[73] The most stable s_A phase of mesogens containing cyano groups is based on layers containing dimers of mesogens. On cooling, the nematic phase formed directly from the isotropic phase contains both dimeric mesogens and monomeric mesogens and so does the first s_A phase. In order to go from the less ordered s_A phase to the s_A phase based on dimeric mesogens, a n_{re} phase is required (Figure 11).[73]

MONOMER   DIMER

SMECTIC C   SMECTIC A   NEMATIC   ISOTROPIC

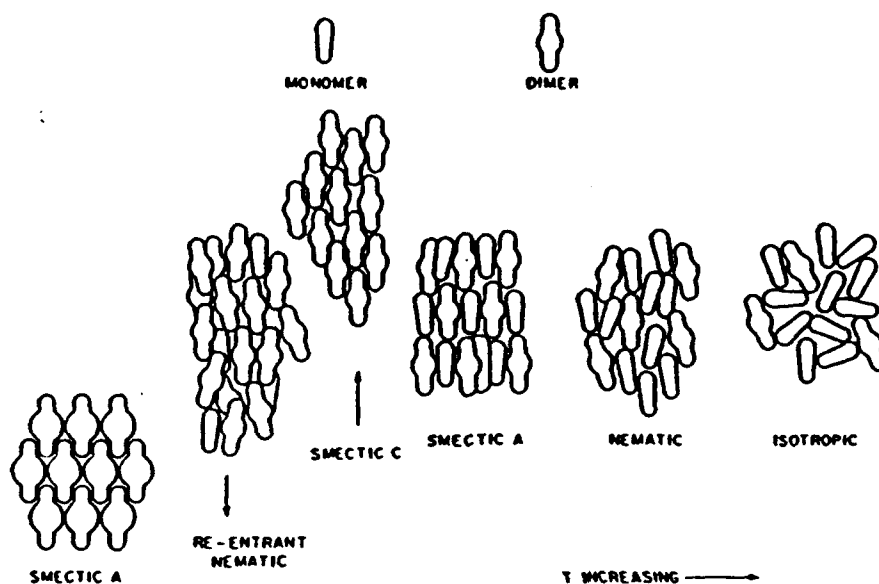RE-ENTRANT NEMATIC

SMECTIC A   T INCREASING ———►

Figure 11. The mechanism of formation of the re-entrant nematic mesophase.

LIQUID CRYSTALLINE POLYMERS CONTAINING CROWN ETHERS AND POLYPODANTS

Mesomorphic host-guest systems of low molecular weight and polymer liquid crystals containing macroheterocyclic ligands and polypodants provide a novel approach to self-assembled systems which combine selective recognition with external regulation.[81-84] Three basic architectures can be considered for liquid crystalline polymers containing crown ethers (Figure 12): main chain liquid crystalline polymers containing crown ethers in the main chain of the polymer and side chain liquid crystalline polymers containing crown ethers either in the mesogenic group or in the main chain. Alternatively, the same series of polymers with polypodants instead of crown ethers can be considered.

Main chain polyamides and polyethers containing crown ethers were reported.[85,86] A variety of side chain liquid crystalline polymers containing crown ether groups at one end of the mesogenic unit were designed.[87-93] Side chain liquid crystalline polymers containing crown ethers in the main chain were synthesized by living cationic cyclopolymerization and cocyclopolymerization of 1,2-bis(2-ethenyloxyethoxy)benzene derivatives containing mesogenic side groups.[94,95] Polymers containing crown ethers in the side groups dissolve ion-pairs and behave as copolymers containing two different mesogenic groups, i.e., complexed and uncomplexed. Their behavior is similar to that of copolymers derived from two different mesogenic groups. Therefore, their phase behavior is directed by molecular recognition.[96] The use of oligooxyethylenic spacers in main chain,[97] and side chain[98-100] liquid crystalline polymers leads to liquid crystalline polypodants. Both main chain[97] and side chain[100] liquid crystalline polypodants dissolve large amounts of alkali metal salts, and the resulting liquid crystalline polyelectrolytes are ionic conductors.[101]

I. Main Chain Liquid Crystalline Polymers
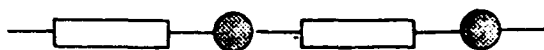
II. Side Chain Liquid Crystalline Polymers

A. Crown ether ligand as part of the mesogenic unit

- crown ether ligand
- mesogenic unit
- interconnecting unit
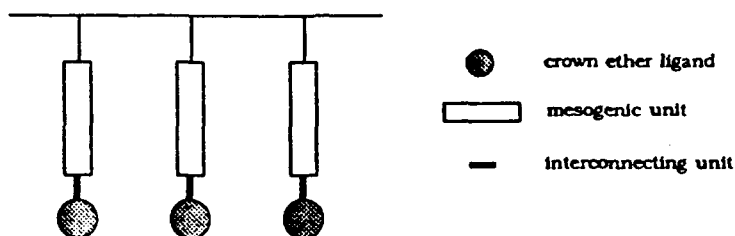
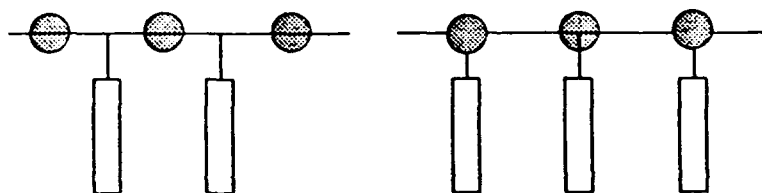B. Crown ether ligand as part of the polymer backbone

Figure 12. The molecular architecture of liquid crystalline polymers containing crown ether ligands.

MOLECULAR RECOGNITION DIRECTED SELF-ASSEMBLY OF SUPRAMOLECULAR LIQUID CRYSTALLINE POLYMERS

The molecular recognition of complementary components leads to systems able to self-assembly or self-organize i.e., systems capable to generate spontaneously a well defined supramolecular architecture from their components under a well-defined set of conditions.[81,82] Although self-assembly is a well recognized process in biological systems,[102,103] the general concept of self-assembly of synthetic molecules by molecular recognition of complementary components, received a revived interest only after it was integrated by Lehn in the new field of supramolecular chemistry.[81,82,104,105] Several examples in which molecular recognition induces the association of complementary nonmesomorphic components into a low molar mass or polymeric supramolecular liquid crystal are described below. The principles of formation of a mesogenic supramolecule from two complementary components is outlined in Scheme 6. The particular example used by Lehn et al.[106] to generate a supramolecular mesogenic group which exhibits a hexagonal columnar mesophase is by formation of an array of three parallel hydrogen bonds between groups of uracil and 2,6-diaminopyridine type as those depicted in Scheme 6. The transplant of the same concept to the generation of a supramolecular liquid crystalline polymer is outlined in Scheme 7.[107] The complementary moieties used TU_2 and TP_2 are uracil (U) and 2,6-diacylamino-pyridine (P) groups connected through tartaric acid esters (T). The tartaric acid (T) unit provides in addition, the opportunity to investigate the effect of changes in chirality on the species formed. Thus the components LP_2, LU_2, DP_2, MP_2 and MU_2 are derived from L(+), D(-) and meso (M) tartaric acid respectively. Although all monomers
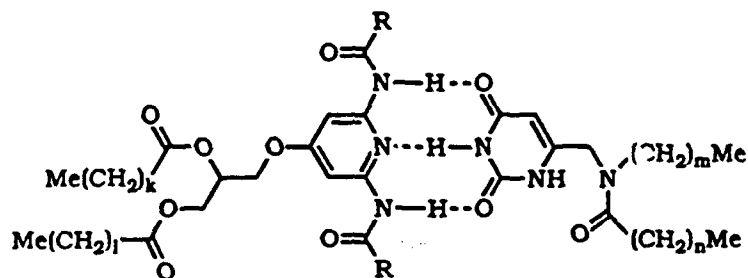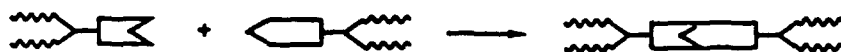
Scheme 6. Formation of a mesogenic supramolecule from two complementary components.
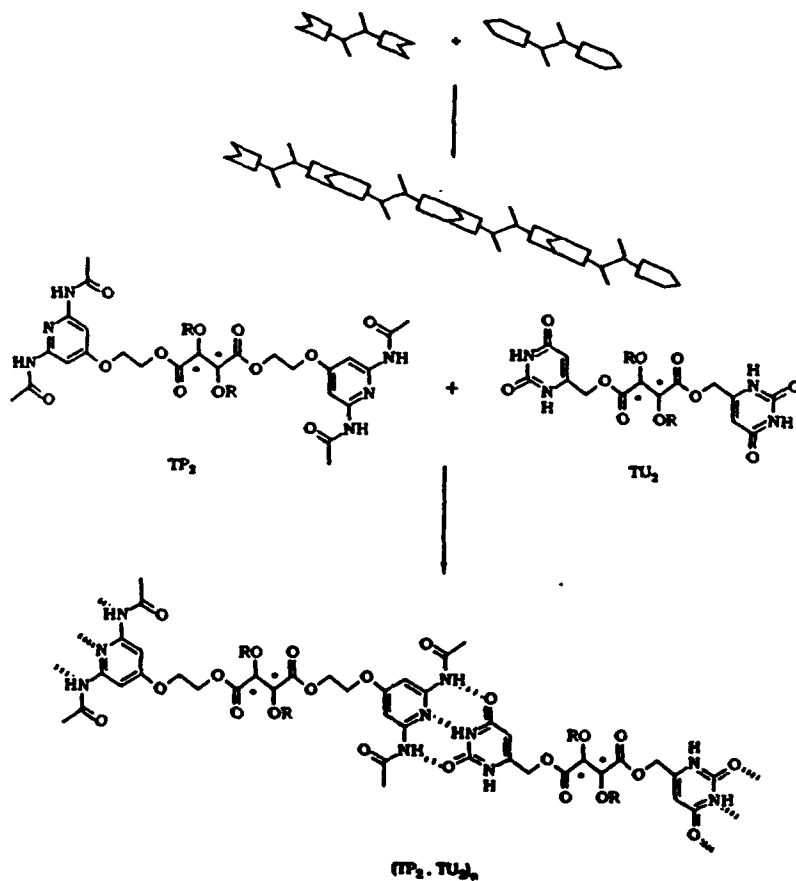
Scheme 7. Generation of a supramolecular liquid crystalline polymer.

(LP$_2$, LU$_2$, DP$_2$, MP$_2$ and MU$_2$) are only crystalline, the corresponding supramolecular "polymers" obtained through hydrogen bonding (LP$_2$ + LU$_2$, DP$_2$ + LU$_2$ and MP$_2$ and MU$_2$) exhibit hexagonal columnar mesophases. These hexagonal columnar mesophases are generated from cylindrical helical suprastructures.[107]

An additional example of supramolecular liquid crystalline polymer obtained through the hydrogen bonding of nonmesomorphic monomers was recently reported.[108] Examples in which a mesophase was generated through dimerization of carboxylic acid derivatives via hydrogen bonding were available in the classic literature on liquid crystals and were extensively reviewed.[109,110] New and interesting examples on the generation of nonsymmetrical liquid crystalline dimers,[111] twin dimer[112] and side chain liquid crystalline polymers[113] by specific hydrogen bonding "reactions" continue to be reported (Scheme 8).
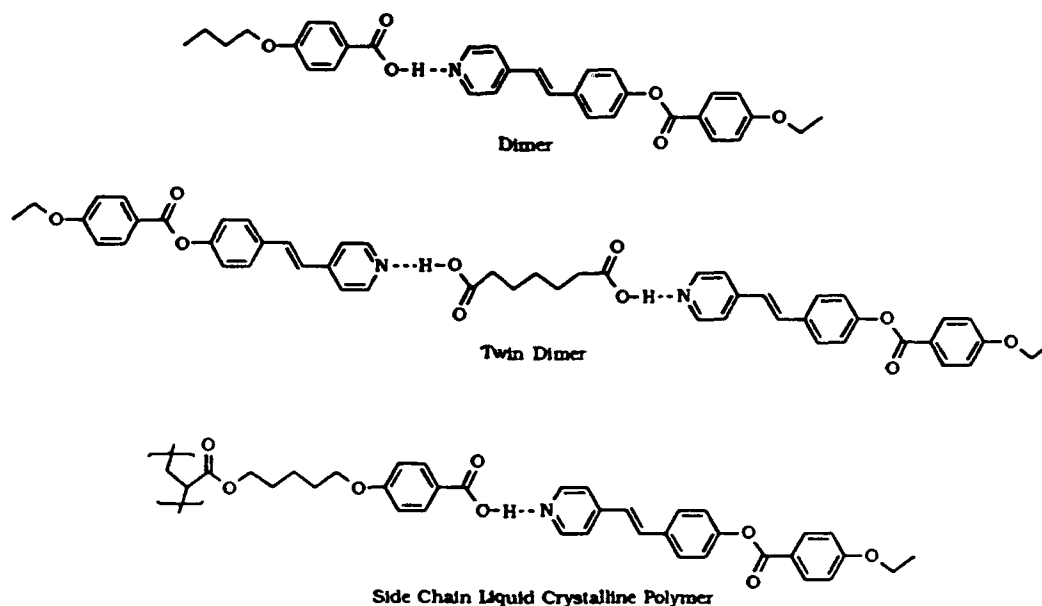
Scheme 8. Generation of nonsymmetrical liquid crystalline dimers, twin dimers and side chain liquid crystalline polymers by specific hydrogen bonding interactions.

Recently, a new approach to molecular recognition directed self-assembly of a liquid crystalline supramolecular structure by a mechanism which resembles that of self-assembly of tobacco mosaic virus (TMV) was reported.[114] The self-assembly mechanism of TMV is outlined in Figure 13.[103] The synthetic approach can be summarized as follows. A flexible polymer backbone containing tapered side groups self-organizes the side groups into a column which surrounds the polymer backbone (Figure 14). These polymers exhibit thermotropic hexagonal columnar mesophases (Figure 15). Although the number of chains
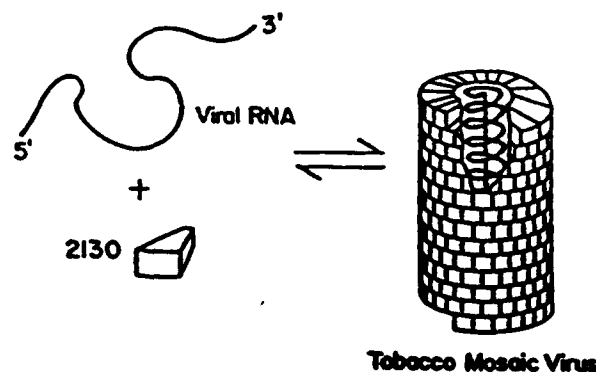
Figure 13. Self-assembly of tobacco mosaic virus (TMV). The protein subunits define the shape of the helix and the RNA defines the helix length. All information for assembly is contained within the component parts.

Figure 14. The self-organization of a randomly coiled flexible
polymer containing tapered side groups into a rigid rod-
like columnar structure.

Figure 15. A representative structure of a flexible polymer
containing tapered side-groups and its self-assembling
into a columnar structure which exhibits a hexagonal
columnar mesophase.

penetrating through the center of the column is not yet known and requires further research (Figure 15), it seems that this self-assembling system is complementary to those elaborated by Lehn et al.[106,107]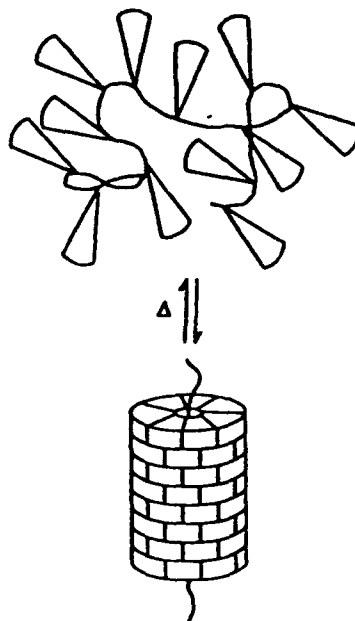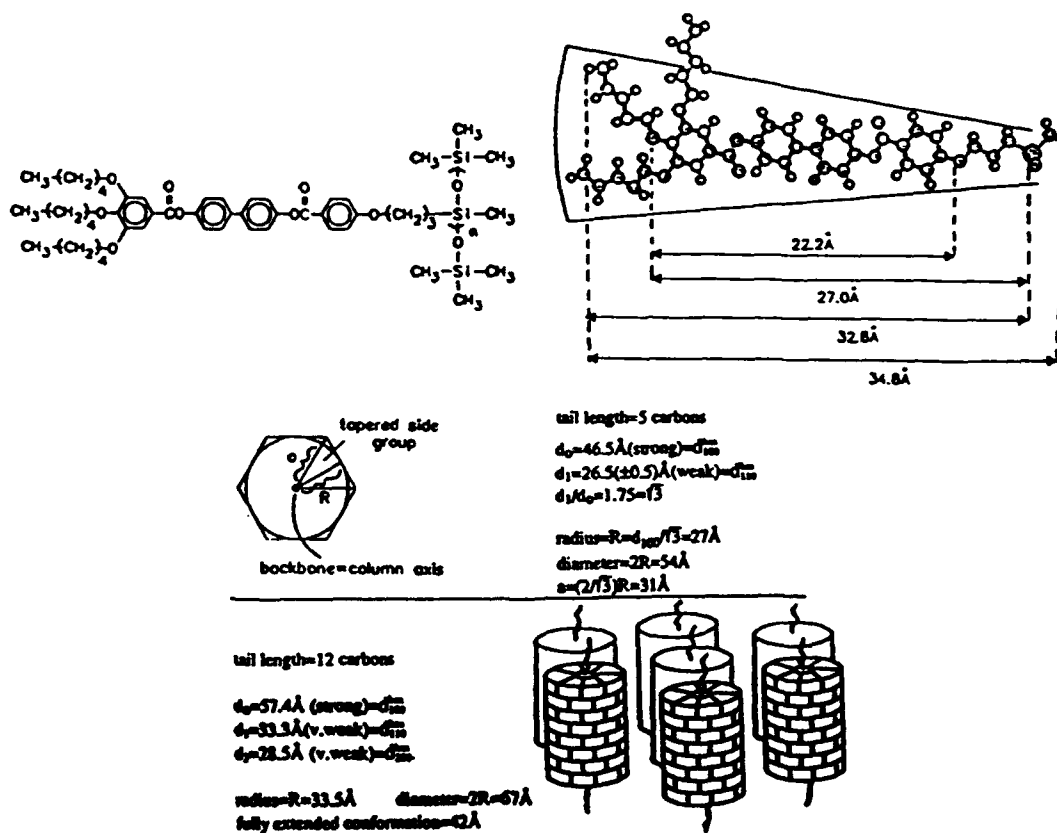 In the model elaborated by Lehn et al.[106,107] the complementary pairs are self-organized through hydrogen bonding type interactions (endo-recognition), while in the last case[103,114] only the shape of tapered side groups is responsible for the generation of a polymeric column (exo-recognition).

ACKNOWLEDGMENTS

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